

# Mechanism of chain folding in polymer crystallization

S. Stepanow

*Martin-Luther-Universität Halle-Wittenberg,*

*Institut für Physik, D-06099 Halle, Germany*

(Dated: May 15, 2013)

## Abstract

I develop a description of polymer crystallization by considering as driving force the repulsion between fluctuational stems, which form below a characteristic temperature  $T_m^0$  due to frequent occupations of trans-states along the chains, and orient in order to minimize the excluded volume. The thickness of stems and bundles is determined by setting equal the average formation time of stems of length  $d_l$  with the Rouse time of a piece of polymer of the same arc length  $d_l$ , and is thus determined by the coil structure of the polymer. The lamella thickness derived in this way is inversely proportional to the supercooling. An expression for the growth rate is derived by considering the growth as a dynamic multistage process. The scattering intensity at the early stage of polymer crystallization is also discussed.

PACS numbers: 61.41.+e, 61.25.H-, 64.70.D-, 81.10.Aj

## I. INTRODUCTION

The understanding of polymer crystallization and its theoretical description in the framework of polymer statistics remains a challenging problem since its discovery [1]-[3]. The classical theories of polymer crystallization [4]-[6] (see also [7]-[9] and citations therein) are based on the nucleation theories developed for low molecular weight systems, and do not make use of key features of polymers in melts and solutions. Despite enormous interest in polymer crystallization over many decades, the molecular mechanism of polymer crystallization is not understood, and a polymer statistics based description is not available. A criticism on the application of nucleation theory to the 2nd crystallization, i.e., crystal growth, exists in the literature (see [10], [22], [37] and citations therein). A review of the research in the field of polymer crystallization in the eighties can be found in [11]. Many important specific features of polymer crystallization were established in the recent research in the field, which includes experimental work [12]-[18], computer simulations [19]-[27], and theoretical studies [28]-[33] (and citations therein). The progress of the experimental and theoretical research in the field of polymer crystallization in recent years is reviewed in [34]-[35].

A new view of polymer crystallization was developed by Strobl [36]-[37], who started from the observation that the nucleation based theories are in disagreement with experiments [38]-[40]. The dependence of the crystallization temperature  $T$  on the inverse lamella thickness  $d_l^{-1}$  has a larger slope than that of the melting temperature, so that these curves intersect at some temperature (comparable with the temperature of zero growth  $T_{zg}$ ), which implies that the polymer crystallization can develop only below  $T_{zg}$ . The picture proposed by Strobl is based on a multistage character of the crystallization process, and the notion of precursor for polymer crystallization without however to specify the statistical mechanical origin of his scenario.

In this article I develop a description of polymer crystallization by considering as driving force the repulsions between fluctuational stems, which form below a characteristic temperature  $T_m^0$  due to favored occupation of the trans states along chains, and orient in order to minimize the excluded volume. The importance of repulsive interactions in this approach is in accordance with the general evidence of the role of repulsive interactions in liquid-solid phase transformations. The van der Waals attractions of formed stems being anisotropic are expected to be more effective in stabilizing the lamellae formation. The lamella thickness

is considered to be the result of a competition between the formation of stems and the coil character of polymer chains. The selection of the lamella thickness  $d_l$  by the ‘microscopic’ time  $\tau_s \sim 10^{-9}$  s according to Eq. (1) has the consequence that  $d_l$  in contrast to the growth rate (characterized by the larger time scale  $t_g$ ) is robust to changes of external parameters except supercooling.

The article is organized as follows. Section II introduces the basic ideas, and presents calculations of the lamella thickness and growth rate. Section summarizes our conclusions.

## II. LAMELLA THICKNESS AND GROWTH RATE

Fluctuational occupations of the trans states in an undercooled polymer melt of interpenetrating chains results in formation of stems possessing a finite lifetime. The repulsion between the neighbor stems forces them to orient in the same direction, and results in formation of bundles. The augmentation of occupations of trans states below a temperature  $T_m^0$  increases the lifetime of stems, and enforces the effect of repulsions. The mutual repulsions between the stems in bundles result in longitudinal thickening of the latter. Van der Waals interactions, which are reinforced due to advancing orientation of stems due to increase of the density, are expected to play a stabilizing role in building of bundles and the lamellae. The orientations of stems due to repulsion between them is similar to the mechanism of the isotropic-nematic transition in lyotropic liquid crystals, where according to Onsager [41] the minimization of the excluded volume is responsible for the transition. The difference between liquid crystals and polymers is that in the case of polymer crystallization the stems do not exist from the beginning, but emerge due to occupation of trans states, and orient and grow due to repulsive interactions between the stems. The present approach is in accordance with simulations in [23]-[24], where chain folding takes place in polymer crystallization by taking into account only repulsive intermolecular interactions. The intramolecular dihedral energies are associated with the differences between, e.g., gauche and trans states, and are responsible for the formation of stems.

The balance between the competing tendencies of stem formation and the coil character of polymers can be expressed by setting equal the inherent time scales of these structures, i.e., the average formation time  $\tau_s$  of stems of the length  $d_l$  and the Rouse time of polymer

pieces of the same length  $d_l$

$$\tau_s = \tau_{Rouse}(d_l). \quad (1)$$

For the average formation time of stems we adopt the following phenomenological expression

$$\tau_s = \frac{d_l}{v_0 + c\Delta T}, \quad (2)$$

where  $\Delta T = T_m^0 - T$  is the supercooling and  $v_0$  and  $c$  are constants. The non-zero value of  $v_0$  accounts for the effect of the presence of an orienting crystal surface on the formation of stems and bundles. Thus, the non-zero value of  $v_0$  is legitimate for secondary crystallization, i.e., crystal growth, and for heterogeneous nucleation at small supercoolings. The Rouse time of a polymer with arc length  $d_l$  is given by

$$\tau_{Rouse}(d_l) = \frac{\zeta d_l^2}{3\pi^2 k_B T_m^0}, \quad (3)$$

where  $\zeta$  is the monomer friction coefficient ( $\zeta \simeq 4.74 \times 10^{-13} \text{Ns/m}$  for polyethylene), and we have replaced  $T$  in (3) by  $T_m^0$ , which is legitimate for small supercooling. The quantity  $k_B T_m^0 / \zeta$  is the monomer diffusion coefficient. The condition (1) taking into account (2) and (3) results in the following relation between the crystallization temperature and the lamella thickness

$$T = T_c^0 - \frac{3\pi^2 k_B T_m^0}{c\zeta} \frac{1}{d_l}, \quad (4)$$

where  $T_c^0 = T_m^0 + v_0/c$ . The condition  $T_c^0 > T_m^0$  is a consequence of the assumption  $v_0 \neq 0$ . The van der Waals attraction of formed stems to the surface is expected also to contribute to the non-zero value of  $v_0$ . The estimate of  $\tau_{Rouse}$  for  $d_l = 15 \text{ nm}$  yields for example for polyethylene the value of order of  $10^{-9} \text{s}$ . The equality of  $\tau_s$  given by Eq. (2) and  $\tau_{Rouse}$  expresses the balance between the isotropic-nematic ordering of emerging stems and the coil structure of polymers, and can be interpreted qualitatively as follows. The stem growth occurs until the parts of a chain outside a bundle, which are also forced to form stems, will be located on the lateral side of the bundle, and will likely belong to the bundle. Thus, the competition between the orientations of stems and the coil nature of the polymer chains yields that the consecutive stems along the polymer will be folded and likely belong to the same bundle. Therefore, the longitudinal growth of the bundles is restricted by the coil structure of polymers, which applies in the Rouse theory on all scales. At larger supercooling, a smaller stem length will be selected as a result of this interplay. The chains in polymer

melts are Gaussian coils irrespective of the presence of entanglements, so that according to the above picture we expect that entanglements weakly influence the condition (1). On the contrary the influence of entanglements on the growth rate is more complex (see [9], Vol II, Sect. 9.14 and [43]). The proposed folding mechanism is expected to apply for both primary and secondary crystallization processes. For primary crystallization, where the surface effect is marginal ( $v_0 \simeq 0$ ), one can apply (4) with  $T_c^0 = T_m^0$ . We expect that the above folding mechanism applies for crystallization from polymer solution too, where the slow collapse due to van der Waals interactions occurs first, which is followed by the fast folding mechanism due to repulsion-orientation coupling after the repulsive interactions become significant as a result of increase of density. We also expect that the above folding mechanism based on trans and gauche conformation states is generic for polymers with more complicated local conformation states.

Eq. (2) yields for the ratio  $G_s = d_l/\tau_s$  the expression  $G_s = v_0 + c\Delta T$ . Because stems at the time scale  $\tau_s$  are expected to form and decompose, the quantity  $G_s$ , which has the dimensionality of growth rate, is a fluctuational quantity, so that the above estimate has to be understood as the average value of  $G_s$ . Eq. (1) implies that the folding length  $d_l$  is selected in the fluctuational regime associated with the ('microscopic') time  $\tau_s$ . Because the Ansatz given by Eq. (1) is local, the lamellae thickness is expected, in contrast to the growth rate, to be robust with respect to changes of external parameters such as molecular weight, etc. This consequence of the Ansatz in Eq. (1) is in accordance with experiments [9].

Since  $T_c^0 > T_m^0$  and the circumstance that crystallization can occur for  $T_c(d_l) < T_m(d_l)$ , the crystallization line, which is described by Eq. (4), has to cross the melting line, which is given by the Gibbs-Thomson relation

$$T = T_m^0 - \frac{2\sigma_e T_m^0}{\Delta h} \frac{1}{d_l}, \quad (5)$$

where  $\Delta h$  is the heat of fusion and  $\sigma_e$  is the surface tension of the fold surface.

The change of supercooling during the crystallization process will result according to the condition (1) in a change of lamella thickness in accordance with observations made long ago [42]. The term  $v_0$  is especially important for small  $\Delta T$ , where the polymer crystallization starts primarily on crystallization seeds and develops in form of spherulites.

The parameters in Eq. (4) can be estimated from the fit to the crystallization line in Fig. 10 of [37]. The ratio  $v_0/c$  is equal to  $T_c^0 - T_m^0$  and possesses for poly- $\epsilon$ -caprolactone

according to Fig. 10 of [37] the value 36 K. The slope of (4), which is obtained as  $\partial T / \partial d_l^{-1} = -3\pi^2 k_B T_m^0 / c\zeta$ , possesses according to [37] the value  $-650$  K nm. Thus, Eq. (4) with constants  $v_0\zeta$  and  $c\zeta$  estimated for poly- $\epsilon$ -caprolactone as  $v_0\zeta \simeq 610 k_B$  and  $c\zeta \simeq 17 k_B$  coincides with the crystallization line in Fig. 10 of [37]. Note that Eq. (4) with  $T_c^0 > T_m^0$  is in accordance with Strobl's analysis of experimental data and can be considered as a theoretical basis for Strobl's experimental observations.

We now will consider the time evolution of formation and deposition of stems in the vicinity of the crystallization front. A self-consistent treatment of the mutual correlations of different stems enables one to consider a time-dependent growth rate of one stem  $G(t)$ . At the time  $t = t_l$ , when on average one stem attaches the crystal surface, the quantity  $G \equiv G(t = t_l)$  is the growth velocity given by the ratio of one attached stem per time  $t_l$ . The multistage character of the growth means that the growth occurs by sequences of processes, and implies that  $G(t + \Delta t)$  depends on  $G(t)$ , which enables one to write down the following phenomenological differential master-type equation for  $G(t)$  as function of time

$$\frac{dG}{dt} = -\gamma G t^{-\alpha}, \quad (6)$$

where  $\alpha < 1$  ( $\alpha = 1/2$  in the following) and  $\gamma$  is a constant. The factor  $t^{-\alpha}$  in (6) takes into account the slow down of the variation of  $G$  with time. The value  $\alpha = 1/2$  is justified by the random character of the attachment process. Eq. (6) is similar to the multiplicative renormalization of quantities from microscopic to macroscopic scales in the theory of critical phenomena in the case when the coupling constant does not renormalize [44]. Because Eq. (6) is intended to describe the growth rate of one stem it should be integrated from  $t = 0$  until the time  $t = t_l$ , which corresponds to formation and attachment time of one stem to the crystal surface. The absence of a positive term on the right-hand side of (6) ensures that (6) does not possess a steady state solution. Note that master-type equations for crystal growth (see e.g. [8]) describe many stems growth, and do possess a steady state solution. The integration of Eq. (6) from  $t = 0$  until the time  $t = t_l$  yields

$$G \equiv G(t_l) = G_0 \exp(-2\gamma\sqrt{t_l}). \quad (7)$$

For comparison, the growth rate for ballistic deposition is independent of  $t$ , while  $G$  for diffusion controlled deposition is proportional to  $t^{-1/2}$ . The above equation suggests that  $t_l$  at the start of crystallization, where the growth rate is zero, is infinite.

A naive identification of  $t_l$  with the time given by the condition (1) yields

$$t_l \simeq \tau_s = \frac{d_l}{c(T_c^0 - T)} = \frac{3\pi^2 k_B T_m^0}{c^2 \zeta} (T_c^0 - T)^{-2}. \quad (8)$$

Eq. (7) with  $t_l \simeq \tau_s$  yields  $G = 0$  at  $T = T_c^0$ . However, as consequence of intersection of the crystallization and melting lines given by Eqs. (4-5) the growth rate is non-zero only below the intersection temperature  $T_{is}$ . The latter is also in accordance with Strobl's analysis of experimental data [37], where the growth rate becomes zero at the temperature  $T_{zg} < T_m^0$ . Thus, to take this circumstance into account we adopt (8) with  $T_c$  replaced by  $T_{zg}$  which yields the time  $t_g$ , which is larger than  $t_l$ . The difference between  $t_l$  and  $t_g$  can be understood as follows: While  $t_l$  ( $\simeq \tau_s$ ) gives the selection rule for lamella thickness from the comparison of time scales of competing processes (i) stem formation and (ii) coil shape of polymers, and does not make a statement on the time course of the growth process, the time  $t_g$  is associated with the real time of formation and attachment of a stem at the crystal surface by taking into account the complicated dynamics, and is therefore much larger than  $t_l$ . Note that the orientation time of stems is not included in  $t_l$ , but in  $t_g$ . Inserting  $t_g$  for  $t_l$  in (7) we arrive at the following estimate of the growth rate

$$G = \tilde{G}_0 \exp \left( -\frac{a}{T} - 2\gamma \sqrt{\frac{3\pi^2 k_B T_m^0}{c^2 \zeta}} \frac{1}{T_{zg} - T} \right), \quad (9)$$

where  $G_0 = \tilde{G}_0 \exp(-a/T)$  is introduced to take into account the increase of the relaxation time (viscosity) with decrease of temperature. It follows from Eq. (9) that  $G$  possesses a pronounced maximum as a function of  $T \leq T_{zg}$ . Note that in contrast to the Turnbull-Fisher expression [45] for  $G$  in nucleation theory, the above expression describes the attachment rate of one stem. To obtain the experimentally measured growth rate one should multiply (9) with the average number of stems formed per time and per volume. The quantity  $(2\gamma/\sqrt{c})\sqrt{3\pi^2 k_B T_m^0/c\zeta} = 51\gamma/\sqrt{c}$  is equal to the characteristic temperature  $T_G$  appearing in the growth rate  $u = u_0 \exp(-T_A^*/T - T_G/(T_{zg} - T))$  given by Eq. (6) in [47]. The fit for poly- $\epsilon$ -caprolactone yields  $T_G = 397^\circ C$ , so that one obtains  $\gamma/\sqrt{c} \simeq 7.8$ .

Note that the existence of two separated time scales  $\tau_s$  and  $t_g$ , which have a clear physical meaning in the present approach, is in accordance with the experimental finding that the growth rate depends exponentially on  $t_g$  and  $\gamma$ , which is expected to depend considerably on external parameters such as pressure, molecular weight, entanglements, etc. [9], while

the lamella thickness is determined by the ‘microscopic’ time  $\tau_s$ , which, as it follows from the definition, is insensitive to the external parameters.

The relation between the proposed folding mechanism of polymer crystallization and the isotropic-nematic transition in liquid crystals [46] permits to make the following qualitative predictions on the behavior of the scattering function at the early stage of polymer crystallization. In approaching the critical point of the isotropic-nematic transition the scattering function increases, remains however finite because the isotropic-nematic transition is of 1st order, and homogeneously decays with the scattering vector  $q$ . The increase of the length of stems drives the system to the phase transition so that the scattering function in polymer crystallization will consequently increase with time at the early stage of polymer crystallization. However, in contrast to liquid crystals, the fluctuational folds in undercooled polymer melts, which occur at times given by Eq. (1) with  $v_0 = 0$  and smaller times, are expected to be responsible for the shift of the maximum to finite  $q$ . The comparison of (2) with  $v_0 = 0$  and  $v_0 > 0$  yields that the characteristic length of fluctuational folds is larger than  $d_l$ . It is likely that the fluctuational folds will be seen at the early stages of polymer crystallization in SAXS peak at  $q \simeq 2\pi/d_l$ . This prediction of the present approach is in accordance with experimental results [12]-[13], where, however, the results are interpreted using the spinodale decomposition theories [29].

### III. CONCLUSIONS

To summarize, I developed a description of polymer crystallization in which the chain folding is determined by the competition between the stem formation, which is the consequence of preferential occupations of trans states in the undercooled polymer melt, their orientation to minimize the excluded volume, and the coil shape of polymer chains. The present approach suggests that the selection of lamella thickness in polymer crystallization is of kinetic origin, and is determined by the ‘microscopic’ time scale  $\tau_s$ . The growth rate for formation and deposition of one stem at the growing surface is derived from the differential master-type equation for the scale dependent attachment rate of one stem, which incorporates the multistage character of the secondary crystallization. The proposed scenario predicts an increase of the scattering intensity with time at the early stages of polymer crystallization. It would be very insightful to compute the three phenomenological constants

$v_0$ ,  $c$ , and  $\gamma$  via microscopic theories or computer simulations.

### Acknowledgments

I acknowledge partial financial support from the German Research Foundation, Ste 981/3-1 and SFB TRR 102. I am grateful to W. Paul, K. Saalwächter, C. Schick, and T. Thurn-Albrecht for useful discussions.

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